NATIONAL BUREAU OF STANDARDS REPORT

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THERMAL CONDUCTIVITY OF SEMICONDUCTIVE SOLIDS;
METHOD FOR STEADY-STATE MEASUREMENTS ON
SMALL DISK REFERENCE SAMPLES

Interim Technical Report
Covering Period
April 1, 1961, to August 31, 1962

by

D. R. Flynn

Report to the
Bureau of Ships
Department of the Navy
Washington, D. C.

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U. S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

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TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

TABLE OF CONTENTS (Cont'd)

APPENDIX A

THERMAL CONDUCTIVITY OF SEMICONDUCTIVE SOLIDS; METHOD FOR STEADY-STATE MEASUREMENTS ON SMALL DISK REFERENCE SAMPLES

by

D. R. Flynn

ABSTRACT

An absolute cut-bar method of measuring the thermal conductivity of solids is described, suitable for small specimens of semiconductive materials. Measurements have been made at temperatures from 200° to 1200°C on a nickel-chromium alloy (Inconel 702) and a 60% platinum-40% rhodium alloy. Measurements have been made to 1000°C on a microcrystalline glass (Pyroceram 9606). Additional measurements are intended.

1. INTRODUCTION

The thermal conductivity of thermoelectric materials is of great importance in determining the performance of a thermoelectric device. If such a device is to have a high efficiency, the thermal conductivity of the thermoelectric elements must be as low as possible in the temperature range in which they are to operate. Reliable thermal conductivity data are required at temperatures ranging from below room temperature to 2000°C, since it is advantageous to operate a thermoelectric generator at as high a temperature as possible.

Reliable thermal conductivity data at elevated temperatures are not generally available, partly because of the difficulties of making such measurements. Many semiconductor materials of interest are available only in small samples, because of the difficulty of obtaining them with adequate uniformity. Consequently, it is necessary that a method of measuring the thermal conductivity of such materials be one suitable for small specimens and capable of use at high temperatures.

It is the purpose of this investigation to develop a method and apparatus for steady-state thermal conductivity measurements at temperatures to 800°C and above, and suitable for solids in the form of small specimens (1/2-in. by 1-in. diameter disks), with the objective of providing samples for

use by other laboratories as thermal conductivity reference specimens in connection with their measurements on solid semiconductors.

A previous report [1]<u>1/</u> gave a summary of the findings of this investigation during the two-year period from February 23, 1959, to March 31, 1961. For the convenience of the reader, the abstract of this earlier report is reproduced in Appendix A.

The present report describes the high temperature model of the absolute cut-bar apparatus, the design of which was based on experience gained using the modified prototype apparatus described in reference [1]. A summary is given of the findings of this investigation to date.

2. DESCRIPTION OF ABSOLUTE CUT-BAR METHOD

2.1. Apparatus

The general assembly of the thermal conductivity apparatus is shown in figure 1. The 2.54-cm diameter specimen was interposed between a hot bar and a cold bar, which were fabricated from 60% platinum-40% rhodium alloy. These bars were supported by an alumina tube from below and an alumina rod from above. Surrounding the inner assembly and concentric with it was an alumina guard cylinder, which was in turn surrounded by a stainless steel case. The space inside the lower alumina support tube, that between the central assembly and the guard cylinder, and that between the guard cylinder and the outer case were filled with finely divided alumina powder as thermal insulation.

The desired temperature distributions within the apparatus were attained with the aid of a number of heaters, each of which were fabricated from 80% platinum-20% rhodium alloy wire.

    a. The cold bar was brought to a desired temperature by means of a small heater fabricated from 0.25-mm diameter wire wound in a helical groove around the alumina bar immediately above the cold bar.

    b. The hot bar was raised to the desired temperature above the cold bar by means of a small disk-shaped heater between the hot bar and the lower alumina

1. Figures in brackets indicate the literature references at the end of this report.

support tube. This heater was fabricated from
0.25-mm diameter wire and had a resistance of
approximately 2 ohms (at room temperature).

c. In order to minimize heat losses down the support
tube from the hot bar heater, a small heater,
fabricated of 0.25-mm wire, was wound on the
support tube at a position about 4 cm below the
hot bar.

d. A helical groove on the outer surface of the guard
cylinder was wound with two separate heaters of
0.5 mm wire. Between the heaters, the guard cylin-
der wall thickness was reduced to permit a longi-
tudinal temperature distribution along the guard
cylinder corresponding to that along the inner
assembly. A tap divided each of these heaters
into two sections which could be controlled
separately.

Temperatures in the system were determined by means of
platinum-10% rhodium:platinum thermocouples, which were fabri-
cated from 0.38-mm (unless otherwise stated) reference grade
thermocouple wire that had been calibrated by the NBS
Temperature Physics Section. Thermocouple positions are shown
in figure 1. There were two thermocouple stations in the hot
bar and two in the cold bar. In the hot bar support tube
there were two thermocouple stations and one differential
thermocouple. Eight thermocouples were installed to define
the temperature distribution along the guard cylinder. The
number and location of specimen thermocouples were determined
by the nature and geometry of the specimen.

2.2. Instrumentation

Power for the two guard heaters and the cold bar heater
was supplied by variable voltage transformers, which in turn
were fed by a voltage regulating transformer. The cold bar
heater and the guard heater sections nearest the plane of the
specimen were individually regulated by thermocouple-actuated
controllers. The guard heater sections remote from the plane
of the specimen were manually adjusted.

The hot bar heater, which provided the power flowing
through the specimen, was powered by a 28-volt, 4-ampere
regulated d-c power supply with a small bank of power resistors
in series for adjusting to the desired heater current.

The heater in the hot bar support tube had to be closely
regulated, in order to prevent heat gains or losses from the

hot bar heater along the support tube. Using a small d-c
potentiometer, a bias was placed on the signal from a mul-
tiple junction differential thermocouple located in the hot
bar support tube. The resultant signal was amplified by a
breaker-type d-c amplifier and fed into a d-c recorder. The
error signal from the control slidewire in the recorder was
fed into a current-adjusting-type proportional controller
incorporating automatic reset control and rate control. The
output of this unit regulated a magnetic amplifier which fed
power to the heater. The operation of a control system of
this type has been described in detail by West and Ginnings [2].

The noble metal leads of the thermocouples were brought
to an isothermal zone box at room temperature. A thermocouple
with one junction in the zone box and one in an ice bath was
placed in series with a double-pole selector switch, so that
each measuring thermocouple was automatically referenced
against the ice bath [3]. The zone box was also wired to
enable determination of the emf developed between similar
leads of different thermocouples in the hot bar, in the speci-
men, and in the cold bar. For these determinations, a separate
double-pole selector switch with no ice bath in series was
used.

Thermocouple emfs were read on a calibrated precision
potentiometer, usually to 0.1 μv for thermocouples in the
specimen and the hot and cold bar, and to 1.0 μv for thermo-
couples in the guard cylinder. Power input to the hot bar
heater was determined by measuring the d-c current through
the heater and the voltage drop across potential taps located
midway between the differential thermocouple junctions in the
hot bar support. These measurements were made using cali-
brated shunt and volt boxes and measuring their output
voltages by means of the precision potentiometer.

3. ANALYSIS OF METHOD

3.1. Determination of Heat Flow

The heat generated in the hot bar heater could flow, if
permitted, in several directions (see figure 1).

   a. up the hot bar, through the specimen, and into the
      cold bar,

   b. down the hot bar support column,

   c. across the convex surfaces of the hot bar and the
      specimen.

Ideally, the heat should flow entirely through the specimen.
The heat flows b and c should therefore be minimized.

The heat flow up or down the hot bar support column was minimized by keeping the platinum-10% rhodium:platinum differential thermocouple located in the column as nearly as possible at a zero reading. For tests in which the reading of the differential thermocouple was not zero, a correction was made for the slight heat flow through the support column.

The heat flow across the convex surface of the hot bar, specimen, and cold bar was analyzed by solution for the heat flow in the hollow cylinder of powder insulation with prescribed temperature boundary conditions. This analysis was utilized to determine the net heat flow across the inner surface of the hollow cylinder, taking place up to various longitudinal positions of interest on the assembly (i.e., hot bar-specimen-cold bar).

The proper analysis of heat exchanges between the bar assembly and the surrounding powder insulation is essential. Some insight into this problem can be achieved by consideration of a rather crude model. The hot bar, specimen, and cold bar can be thought of as three thermal resistances in series. Shunting each of these resistances is a resistance consisting of a portion of the surrounding powder insulation. For the case in which the thermal conductivity of the specimen is different from that of the bars, there will be a corresponding change in the longitudinal temperature gradient in the adjacent insulation. Since the thermal conductivity of the insulation does not undergo such a change, the insulation must exchange heat with the bars and specimen. In particular, if the specimen has a lower conductivity than the bars, it is necessary for the insulation to steal heat from the bars and specimen on the hotter side and return this heat on the colder side.

A schematic diagram of a cut-bar apparatus (not that described in this report) is shown in the upper left hand corner of figure 2. (The nomenclature used in this diagram refers to a comparative cut-bar apparatus, rather than to an absolute type; the heat flow analysis is the same, however.) The hot and cold bars (meter bars) and the specimen are equal in length; this length is equal to twice their diameter. The radius of the guard has been chosen as 1.5 times that of the bars. For numerical evaluation, the specimen and insulation have been chosen to have, respectively, thermal conductivities 1/5 and 1/100 that of the meter bars.

The graph in the lower left-hand corner of figure 2 illustrates the dimensionless longitudinal temperature distribution that would exist along the meter bars and specimen in the absence of heat exchanges with the insulation. The vertical dashed lines indicate the positions of the interfaces

between the meter bars and the specimen. Since, in this case,
an exactly matched guard is being considered, the temperature
distribution shown is also that which exists along the guard.

The graph in the upper right-hand corner of figure 2
illustrates the dimensionless radial temperature gradient
which exists in the insulation at the convex surface of the
meter bars and specimen. In this particular case, the radial
gradient is substantially zero, except in the regions near the
interfaces. In this graph, the peaks at the interfaces have
arbitrarily been cut off at -1.0 and +1.0. The effect of such
a radial gradient distribution is shown in the graph in the
lower right-hand corner of figure 2. The fractional power
change is plotted versus dimensionless length. The quantity
plotted is the percentage change in power flowing longitudi-
nally through the meter bars and specimen. In this graph,
the power flowing in the first meter bar is seen to remain
constant until the interface is approached. The power drops
rapidly near the interface, then levels off in the specimen
to a constant value approximately 2.2 percent less than that
which was flowing in the first meter bar. Near the second
interface, the longitudinal heat flow increases so that its
rate is the same in the second meter bar as it was in the
first.

It is necessary to originally establish a longitudinal
gradient in the insulation near the hotter bar. In the case
where the bars are quite short, the longitudinal gradient may
not become established, so that heat exchanges occur along the
entire length of the system. Even in the case where the
specimen and the bars have the same conductivity, there may
be heat interchanges along the entire system. In order to
study the parasitic heat flows mentioned, it is necessary to
perform a rather extensive analysis.

Although there may be both radial and longitudinal heat
flows in the powder insulation, it is the radial gradient at
the surface of the bars and specimen that is of particular
interest. In the ideal case, the radial gradient at this
surface would be zero. This is, however, not the case in
general, so that an analysis of the heat flow across this
surface must be made. The heat flow across this surface in
a longitudinal element of area will be

$$dp = 2\pi a k \left(\frac{\partial T}{\partial r}\right)_{r=a} dz \qquad , \qquad (1)$$

where a is the radius of the bars and specimen (cm),
      k is the thermal conductivity of the powder insulation
        (watt/cm deg C),
      T is the temperature in the system (°C),

r is the radial coordinate (cm),
z is the longitudinal coordinate (cm).

The net power flowing across the surface r=a between z=z$_1$ and z=z$_2$ is

$$p_{12} = 2\pi a \int_{z_1}^{z_2} k\left(\frac{\partial T}{\partial r}\right)_{r=a} dz \qquad . \qquad (2)$$

In order to evaluate this integral, it is necessary to have a knowledge of the thermal conductivity of the powder insulation and $(\partial T/\partial r)_{r=a}$ as a function of z. An exact treatment of the system requires solution of the four body composite system involving the two bars, the specimen, and the powder insulation. This has recently been done by B. A. Peavy of the NBS Heat Transfer Section. The resultant solution is very complicated, however, and was not used for the investigation described in this report.

For this apparatus, $(\partial T/\partial r)_{r=a}$ was determined by analysis of the hollow cylinder of powder insulation with its boundaries at known temperatures. The measured surface temperatures along the bars and the guard cylinders were used to establish functions representing the temperatures on the curved surfaces of the region. The ends of the region were assumed to be closed by logarithmic radial temperature distributions, which provide temperature continuity. Axial symmetry was assumed. The analytical solution of the temperature distribution in the region established by these boundary conditions was utilized to evaluate $(\partial T/\partial r)_{r=a}$ in the integral in (2). The thermal conductivity of the powdered alumina insulation was measured in another apparatus [4].

Since the analytical solution of this problem is in the form of an infinite Fourier series, it was necessary to use a digital computer for numerical evaluation of the data. The details of the mathematical development are not amenable to brief treatment and, hence, have been excluded from this report. An unpublished paper giving a fairly detailed analysis of heat flow in the insulation of a simplified cut-bar apparatus was reproduced in an earlier report [5]. It is planned to publish the mathematical analysis of heat flow in a cut-bar thermal conductivity apparatus soon.

The total heat flow through the specimen was determined as

$$Q = P + C\delta + \overline{p} \qquad , \qquad (3)$$

where Q is the total heat (per unit time) flowing in the
      specimen (watt),
   P is the measured heat input (watt),

C is the heat flow up or down the support column due to
a unit temperature difference (watt/deg C),

δ is the temperature difference in the support column
as indicated by the differential thermocouple
(deg C),

$\bar{p}$ is the mean value of the total net heat interchange
with the surrounding insulation for a thermocouple
span in the specimen (watt)(see Eq.(2)).

The measured power input, P, was known very accurately.
The contribution from heat flow in the support column was
minimized by keeping δ small (usually less than 0.1 deg C).
The heaters on the guard cylinder were adjusted to minimize $\bar{p}$.

3.2. Temperature Gradients

Temperatures in the specimens were measured using noble
metal thermocouples, as described above. The particular method
of thermocouple installation varied somewhat with the specimen
being tested, and will be discussed in the appropriate sections
describing experimental results.

Since temperature differences in the specimen were rather
small, it was essential that the conversion of thermocouple
emfs to temperature not introduce any additional uncertainties.
The equation

$$E = 16.82614(\frac{T}{1000}) - 10.30487(\frac{T}{1000})^2 + 7.91246(\frac{T}{1000})^3$$

$$- 2.05305(\frac{T}{1000})^4 - 2.85375(1.0 - \exp[\frac{-4T}{1000}]) \quad , \tag{4}$$

where T is temperature (°C) and E is emf (millivolts), was
found to fit the platinum-10% rhodium:platinum thermocouple
calibration data quite closely over the temperature range 0°
to 1450°C. This equation was used for conversion of all ther-
mocouple voltages to temperature.

3.3. Minimization of Systematic Errors

For all tests, thermal conductivity values were computed
by simultaneous solution of two tests: 1) an "isothermal"
test with no power input to the specimen heater, and 2) a
"gradient" test with sufficient power input to the specimen
heater to maintain the desired longitudinal temperature
gradient. This procedure tends to minimize the effect of cer-
tain systematic errors in temperature or heat flow measurements.

For one-dimensional steady-state heat flow, the total
heat flow, Q, through the specimen is

$$Q = -kA\frac{dT}{dz} \quad , \tag{5}$$

where k is thermal conductivity,
    A is the cross-sectional area of the specimen,
    T is the temperature,
    z is the longitudinal coordinate.

For moderate temperature ranges, the thermal conductivity of the specimen is assumed to vary linearly with temperature; then (5) becomes

$$Q = -k_0 A\{1 + \alpha(T-T_0)\}\frac{dT}{dz} \quad , \tag{6}$$

where k_0 is the thermal conductivity at an arbitrary reference temperature, T_0, and α is its corresponding temperature coefficient.

Integration of (6) yields, assuming Q to be constant,

$$Q = \frac{k_0 A}{L}\Delta T[1 + \alpha(\overline{T}-T_0)] \quad , \tag{7}$$

where

$$\Delta T = T_1 - T_2$$
$$\overline{T} = (T_1 + T_2)/2 \quad , \tag{8}$$

T_1 and T_2 being the temperatures at two positions a distance L apart.

Consider two tests at approximately the same mean temperature; let the heat flow in one test be given by (7) and that in the other test by a similar expression. The difference between these heat flows will be

$$Q-Q' = \frac{k_0 A}{L}[\Delta T-\Delta T' + \alpha\{\Delta T(\overline{T}-T_0) - \Delta T'(\overline{T}'-T_0)\}] \quad , \tag{9}$$

where the primed quantities designate one test and the unprimed quantities designate the other. The expression in braces in (6) can be set equal to zero by proper choice of the reference temperature, T_0.

If
$$T_0 \equiv \frac{\Delta T\overline{T}-\Delta T'\overline{T}'}{\Delta T-\Delta T'} \quad , \tag{10}$$

the thermal conductivity at the indicated reference temperature, T_0, is given by

$$k_0 = \frac{(Q-Q')L}{A(\Delta T-\Delta T')} \tag{11}$$

Equation (11) gives thermal conductivity in terms of the "true" values of heat flows, temperature differences, and dimensions. Now let

$$Q = q - s \qquad\qquad Q' = q' - s$$

$$T_1 = t_1 - \varepsilon_1 \qquad\qquad T_1' = t_1' - \varepsilon_1 \qquad\qquad (12)$$

$$T_2 = t_2 - \varepsilon_2 \qquad\qquad T_2' = t_2' = \varepsilon_2 \qquad ,$$

where the capital letters designate "true" values of the parameters; the lower case t's and q's are the measured values for these parameters; and s, ε_1, and ε_2 are the associated systematic errors. It is assumed that, for two tests at about the same temperature, the systematic errors associated with a particular parameter are the same; experience indicates that this is a good approximation.

From (11) and (12) the thermal conductivity is given by

$$k_0 = \frac{(q - q')L}{A(\Delta t - \Delta t')} \qquad , \qquad\qquad (13)$$

corresponding to the mean temperature

$$T_0 = t_0 + \varepsilon_0 \qquad , \qquad\qquad (14)$$

where

$$t_0 = \frac{\Delta t \bar{t} - \Delta t' \bar{t}'}{\Delta t - \Delta t'}$$

$$\varepsilon_0 = \frac{\varepsilon_2 (t_2 - t_2') - \varepsilon_1 (t_1 - t_1')}{\Delta t - \Delta t'} \qquad\qquad (15)$$

$$\Delta t = t_1 - t_2$$

$$\bar{t} = (t_1 + t_2)/2 \; . \qquad\qquad (16)$$

Equation (13) gives thermal conductivity in terms of the measured values of the parameters, all systematic errors of the type being discussed having been eliminated. The effective mean temperature will be in error by ε_0; however, for most materials the effect of a slight error in mean temperature is negligible.

All thermal conductivity values were computed using (13). The use of this simultaneous solution for computing results significantly improved the precision of the test results and, it is believed, the accuracy as well.

4. RESULTS OBTAINED USING THE HIGH TEMPERATURE ABSOLUTE CUT-BAR APPARATUS

4.1. Platinum-Rhodium Alloy

Measurements were made of the thermal conductivity of the platinum-rhodium alloy from which the hot and cold bars in the high temperature absolute cut-bar apparatus were to be fabricated. It was considered desirable that this be done so that the hot and cold bars could later serve as meter bars to provide a useful check on the heat flow through a specimen interposed between them.

a. Description of Specimen

The specimen used for these determinations was in the form of a right circular cylinder 2.539 cm in diameter and 7.5 cm long with recesses at either end. The solid portion of the cylinder was 6.49 cm long. The geometry of this specimen may be envisaged by reference to figure 1. The specimen was later cut into two pieces which were ground and optically polished to form the hot and cold bars.

The specimen was machined by the manufacturer into the form described. An NBS chemical analysis indicated that the material of the specimen was 60.0 percent platinum and 40.0 percent rhodium by weight.[2] The specimen was annealed at 1000°C prior to the tests described below.

b. Test Procedure

The temperature distribution along the platinum-rhodium alloy specimen was determined by means of four 0.38-mm butt-welded platinum-10% rhodium:platinum thermocouples pressed into 0.3-mm grooves in the convex surface of the bar. The distance between the two extreme thermocouples was 3.94 cm.

Thermal conductivity measurements were made in increasing order of temperature from 200° to 1200°C at 200-degree intervals, and then in decreasing order of temperature at 800° and 400°C. Each conductivity determination involved two tests: (1) an "isothermal" test, in which there was no power input to the specimen heater; (2) a "gradient" test with sufficient power input to the specimen heater to maintain a longitudinal temperature gradient in the specimen of about 2 deg C/cm.

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2. NBS spectrochemical analysis indicated the following impurity elements: Fe 0.01-0.1%; Cu, Ir, Pd, Si, Zr 0.001-0.01%; B, Ca less than 0.001%.

In all of the tests, the guards were adjusted so that there
was very little net heat exchange between the specimen bar
assembly and the surrounding insulation.

c. Results of Thermal Conductivity Tests

The thermal conductivity of the platinum-rhodium alloy
as determined by simultaneous solution of the various pairs
of tests is shown in figure 3. The points plotted are
weighted averages of the values obtained for the three ther-
mocouple spans. Due to uncertainty in the effective distances
between thermocouples, there was some scatter in the individual
values obtained for each span. The average of the three values,
weighted according to the length of each span, retains only
about one-third of this uncertainty.

The circles shown in figure 3 represent measurements
made in increasing order of temperature[3], and the inverted
triangles those made in decreasing order of temperature. The
solid line shown is the quadratic equation of least-mean-
squares fit to all of the data points shown. This equation is

$$k = 0.465 + 0.424 \left(\frac{T}{1000}\right) - 0.151 \left(\frac{T}{1000}\right)^2 \qquad , \qquad (17)$$

where k is thermal conductivity expressed in watt/cm deg C
and T is temperature in °C. The dotted lines shown bound the
region plus and minus 2.2 percent of the conductivity, equiva-
lent to twice the estimated standard deviation divided by the
mean conductivity.

d. Thermoelectric Power

When the 60% platinum-40% rhodium alloy bar was purchased,
a 0.5-mm wire was drawn by the manufacturer from the same
material. A thermocouple fabricated from a length of this
wire and a length of 0.38-mm reference grade platinum wire was
calibrated by the NBS Temperature Physics Section over the
temperature range 0° to 1100°C. The equation

$$E = 13.25682\left(\frac{T}{1000}\right) - 2.76979\left(\frac{T}{1000}\right)^2 + 6.09233\left(\frac{T}{1000}\right)^3$$

$$- 1.79519\left(\frac{T}{1000}\right)^4 - 1.80269\left(1.0 - \exp\left[\frac{-4.5T}{1000}\right]\right) \qquad , \qquad (18)$$

---

3. Prior to the tests shown in figure 3, the specimen was
    annealed in place at 1000°C; hence the designations
    "second heating" and "second cooling."

where E is emf (millivolts) and T is temperature (°C), was found to fit the calibration data quite closely.

Differentiation of equation (18) gives

$$\frac{dE}{dT} = 13.257 - 5.540(\frac{T}{1000}) + 18.277(\frac{T}{1000})^2$$
$$- 7.181(\frac{T}{1000})^3 - 8.112 \ \exp\left[-\frac{4.5T}{1000}\right]$$

(19)

as the thermoelectric power (μv/deg C) of 60% platinum-40% rhodium:platinum.

Similarly, differentiation of (4) gives

$$\frac{dE}{dT} = 16.826 - 20.610(\frac{T}{1000}) + 23.737(\frac{T}{1000})^2$$
$$- 8.212(\frac{T}{1000})^3 - 11.415 \ \exp\left[-\frac{4T}{1000}\right]$$

(20)

as the thermoelectric power (μv/deg C) of 90% platinum-10% rhodium:platinum.

The solid lines in figure 4 show the thermoelectric power of 60% platinum-40% rhodium and 90% platinum-10% rhodium against platinum, as computed from (19) and (20), respectively. From the "Law of Intermediate Metals" [6] it follows that the thermoelectric power of 60% platinum-40% rhodium versus 90% platinum-10% rhodium can be obtained by subtracting equation (20) from (19); the thermoelectric power of this combination is indicated by the dotted line in figure 4.

For each of the tests presented in figure 3, for both the upper and lower thermocouple spans of the specimen, emfs were measured between the respective platinum wires of the two thermocouples and between the respective platinum-10% rhodium wires. Thus, the 60% platinum-40% rhodium bar served as the central portion of four differential thermocouples. From the emf outputs of these differential thermocouples and from the temperature differences, as indicated by the four platinum-10% rhodium:platinum thermocouples, the thermoelectric power of the specimen against 90% platinum-10% rhodium and against platinum was computed. The effects of systematic errors were minimized by simultaneous solution of the "gradient" and "isothermal" tests. In figure 4, the plotted points give the average values obtained for thermoelectric power as a function of temperature. The circles and triangles correspond to

the similar symbols in figure 3 at the same temperatures.
It can be seen that the measured values agree quite well with
the curves obtained from equations (19) and (20).

4.2.   Nickel-Chromium Alloy

Measurements were made of the thermal conductivity of a
nickel chromium alloy (Inconel 702) which previously had
been measured in two models of the NBS metals apparatus [7],
in the NBS modified prototype absolute cut-bar apparatus [1],
and in the NBS steam calorimeter apparatus [8]. Determinations
made on this specimen material served a dual purpose: (1) since
the thermal conductivity of this alloy was already known over a
large temperature range, measurements on this material enabled
a scrutiny of the accuracy of the high temperature absolute
cut-bar apparatus; and (2) they provided additional measurements
to elevated temperatures on a metal which appears suitable for
use as a thermal conductivity reference material.

a.   Description of Specimen

The specimen used for these determinations was in the
form of a cylindrical bar nearly identical in size and shape
to the platinum-rhodium alloy specimen described above (4.1.a).

The specimen was machined at NBS from the same solution-
annealed hot-rolled plate as were the specimens previously
measured in several other NBS apparatus. An NBS chemical
analysis indicated that the alloy was composed of Ni 79.3%,
Cr 17.0%, Al 2.5%, and several other constituents in quan-
tities less than 1 percent (by weight). The detailed analysis
is given in Table 2, along with analyses of several similar
alloys which will be discussed later.

b.   Test Procedure

Temperatures along the specimen were determined by means
of four thermocouples installed in a similar manner to those
in the platinum-rhodium alloy (4.1.b)

Thermal conductivity measurements were made at 200°C, in
increasing order of temperature at 100 degree intervals from
400° to 1200°C, and then in decreasing order of temperature at
900°, 600°, and 300°C. Following preliminary analysis of these
data, an additional series of tests was conducted in which
measurements were made in increasing order of temperature at
200°C and 300°C, at 50 degree intervals from 400° to 700°C,
at 100 degree intervals from 800° to 1200°C, and then in
decreasing order of temperature at 900°, 600°, and 300°C.

Each conductivity determination involved two tests: (1) an "isothermal" test, and (2) a "gradient" test with sufficient power input to the specimen heater to maintain a longitudinal temperature gradient in the specimen of about 4 or 5 deg C/cm.

c. Results of Thermal Conductivity Tests

The Inconel 702 alloy from which the specimen was fabricated was solution-annealed by the manufacturer prior to purchase by NBS. The reported solution treatment for this alloy is to hold the material at 1975°F (1080°C) for one hour, followed by rapid air cooling. If this alloy is held at temperatures in the range from about 650° to 900°C, age hardening will occur due to precipitation of gamma-prime particles from the super-saturated solid solution. The size of the precipitate is highly dependent on the aging temperature. After 900°C aging, the gamma-prime particles are quite coarse, having a maximum diameter of several thousand Å; if the solution-annealed alloy is aged only at lower temperatures, the precipitate is more abundant and finer in size and cannot be resolved by the light microscope.

In the course of the thermal conductivity determinations being discussed, the specimen was cycled twice between room temperature and 1200°C. Since the microstructure of this alloy is dependent on thermal history, the thermal conductivity of the specimen might also be expected to change somewhat, due to heat treatment. At the onset of the measurements, the specimen was in the solution-annealed state, with the gamma-prime phase in supersaturated solution. After the specimen was heated above about 650°C, the gamma-prime phase presumably began to precipitate. As the temperature was further increased, this precipitate became much coarser. Above about 1000°C the precipitate again went into solution. After completion of testing to 1200°C, the specimen was cooled to 900°C, at which time a coarse precipitation occurred. Thus, for the first heating cycle, the specimen was in the solution-annealed state up to about 650°C; from 650° to 900°C, the gamma-prime precipitate was fine at the lower temperatures and became coarser as the temperature was increased; from 1000° to 1200°C, the gamma-prime phase was again in solution. For all of the other tests (first cooling, second heating, second cooling), there was a coarse precipitate at 900°C and below. Since the exact temperatures corresponding to precipitation or solution are not known, the temperatures mentioned should be considered approximate.

The thermal conductivity of the nickel-chromium alloy as determined by simultaneous solution of the various pairs of

tests taken during the first heating cycle is shown in figure
5. The points plotted are weighted averages of the values
obtained in each pair of tests for the three thermocouple
spans. The solid line shown is the cubic equation of least-
mean-squares fit to all the data points. This equation is

$$k_S = 0.1198 + 0.07387(\frac{T}{1000}) + 0.1915(\frac{T}{1000})^2 - 0.08265(\frac{T}{1000})^3 \quad (21)$$

where k_S is thermal conductivity (watt/cm deg C) of the
solution-annealed alloy and T is temperature (°C). To enable
closer scrutiny of the deviations of individual determinations
from the curve, these are shown in figure 6 as percent depar-
tures from the smooth curve plotted against temperature. The
dotted lines bound the region plus and minus two standard
deviations (estimated) from the solid curve. The maximum
departure of any data point from the solid curve is 0.6 per-
cent.

The thermal conductivities obtained when the specimen was
in an age-hardened condition can be represented by the equa-
tion

$$k_a = 0.1179 + 0.1149(\frac{T}{1000}) + 0.1173(\frac{T}{1000})^2 - 0.05008(\frac{T}{1000})^3 \quad (22)$$

in the same units as above. This equation is that of least-
mean-squares fit to the data points obtained during the second
heating and second cooling. The deviations of individual
determinations are shown in figure 7 as percent departures from
smooth curve (22) plotted against temperature. The dotted lines
again bound the region plus or minus two standard deviations
(estimated, using data from second heating and cooling tests
only).

The apparent difference between the thermal conductivity
of this alloy in the solution-annealed state and that in the
age-hardened state is shown in figure 8. The quantity plotted
is $100(k_S/k_a-1)$, where k_S and k_a are given in equations (21)
and (22), respectively. Below 600°C, the alloy in the solution-
annealed condition has a thermal conductivity 2 or 3 percent
less than that in the age-hardened condition. Above 1000°C,
there should be no significant difference between k_S and k_a;
the apparent 1 percent increase of k_S over k_a in this range
is probably due to experimental uncertainty.

The smoothed results of these determinations are tabulated
in table 1 at 100 degree C intervals over the temperature range
200° to 1200°C. The results obtained for solution-annealed

Inconel 702 are given in the second column; those for the age-hardened alloy are given in the third column. Results obtained by several other methods on specimens cut from the same plate of nickel-chromium alloy are included in table 1 for comparison. The data presented in the fourth column were obtained by means of the modified prototype absolute cut-bar and are discussed in a previous report [1]. The tabulated values are those from the quadratic equation of least-mean-squares fit through data points for peened thermocouples only (see [1]). The data in the fifth column represent the manually smoothed data from numerous runs on two specimens of the alloy in two models of the NBS metals apparatus [7]. The sixth column presents data obtained on a specimen six inches in diameter and one inch thick in the NBS steam calorimeter apparatus [8][4]. Indication is given in table 1 as to the probable condition of the alloy (i.e., solution-annealed or age-hardened for each set of data).

TABLE 1

Thermal Conductivity of a Nickel-Chromium Alloy
(Inconel 702) by Several Independent Methods at NBS

Temp., °C	This Investigation		Prototype Absolute Cut-Bar	Metals Apparatus	Steam Calorimeter
	(solution-annealed)	(age-hardened)	(solution-annealed)	(solution-annealed)	(age-hardened)
-150	-----	-----	-----	0.099	-----
-100	-----	-----	-----	.103	-----
0	-----	-----	-----	.114	-----
100	-----	-----	-----	.127	-----
200	0.142	0.145	0.142	.142	-----
300	.157	.162	.159	.158	-----
400	.175	.179	.177	.176	-----
500	.194	.198	.197	.196	-----
600	.215	.218	.217	.218	0.213
700	.237	.239	.238	-----	.235
800	.259	.259	.260	-----	.258
900	.281	.280	-----	-----	.280
1000	.303	.300	-----	-----	.303
1100	.323	.320	-----	-----	-----
1200	.341	.338	-----	-----	-----

4. The data presented in Table 1 for the NBS steam calorimeter are preliminary and may vary slightly from values to be given in the published paper.

Since all of the results presented in table 1 are from
this laboratory, results obtained on similar alloys by an
independent laboratory may also be of interest. Powell and
Tye of the National Physical Laboratory recently reported a
series of measurements on a group of nickel-chromium alloys
somewhat similar in composition to the alloy being investi-
gated at NBS. The chemical composition of the NBS alloy is
presented in table 2 along with the composition of three of
the NPL alloys.

TABLE 2

Chemical Compositions of Four Nickel-Chromium Alloys

	Composition, weight percent									
	Ni	Cr	Al	Ti	Fe	Si	Cu	Co	Mn	C
NBS Alloy	79.3	17.0	2.5	0.59	0.36	0.19	0.14	0.08	0.04	0.066
Nimonic 75	77.9**	20.53	----	.23	.12	.79	.06	----	.27	.126
Nimonic 80*	73.7**	21.0	1.2	2.5	.5	.5	----	----	.6	.04
Nimonic 90	58.9**	19.5	1.4	2.45	.41	.65	.14	16.5	.03	.06

* Nominal composition
** By difference

Table 3 presents tabulated thermal conductivity values for
the NBS alloy as determined by this investigation and for the
NPL alloys as reported [9]. Inspection of table 3 reveals that
the thermal conductivity values for the four alloys have a
range, at any given temperature, of about 13 percent at the
lower temperatures and that the values converge at higher tem-
peratures such that the range at 800°C is only 3 percent.

TABLE 3

Thermal Conductivity of Four Nickel-Chromium Alloys

Temp., °C	Inconel 702 (solution-annealed)	(age-hardened)	NPL Nimonic 75	NPL Nimonic 80	NPL Nimonic 90
200	0.142	0.145	0.157	0.138	0.146
300	.157	.162	.175	.155	.165
400	.175	.179	.191	.168	.184
500	.194	.198	.210	.184	.200
600	.215	.218	.226	.210	.218
700	.237	.239	.243	.235	.237
800	.259	.259	.260	.255	.253
900	.281	.280	----	.276	----

d. Thermoelectric Power

For each of the tests presented in figures 5, 6, and 7, emfs were measured between similar legs of the thermocouples in the specimen (see 4.1.d). Using these data, the thermoelectric power of the specimen against 90% platinum-10% rhodium and against platinum was computed. The analysis has not yet been completed; preliminary results indicate that temperature differences were measured quite accurately. The thermoelectric power of Inconel 702 appeared to be significantly different in the solution-annealed state from that in the age-hardened condition, and may provide a means of ascertaining the condition of the alloy in the tests discussed.

4.3. Microcrystalline Glass

Measurements were made of the thermal conductivity of a microcrystalline glass (Pyroceram 9606; product of Corning Glass Works, Corning, New York). This material was selected with the hope that it would come close to meeting the following criteria:

1. It should have a thermal conductivity in the range 0.01 to 0.05 watt/cm deg C, comparable to thermal conductivities of thermoelectric materials.

2. It should be homogeneous and isotropic so that a variety of sizes and shapes of specimens can be made up from one large stock of the material with confidence that all will have the same thermal values.

3. It should be stable up to 1200°C or higher.

4. It should be opaque to thermal radiation up to at least 1200°C.

5. Its cost should not be excessive.

Microcrystalline glass is first formed as a homogeneous glass (incorporating a nucleating agent) which is transparent, so that any defects can be readily detected visually. By suitable heat treatment, the glass is later converted (by Corning) to a polycrystalline solid which is opaque as a result of the large number of very small crystals. The properties of such materials have been described in the literature [10,11].

Pyroceram 9606 appears to meet the above criteria
fairly well, the biggest uncertainty being its stability
in the range 800° to 1200°C. There appears to be a small
slow change in dimension at the high temperatures, but there
is a reasonable possibility that this may not affect signi-
ficantly the thermal conductivity.

The thermal conductivity of Pyroceram 9606 was measured
in the prototype absolute cut-bar apparatus and the results
reported previously [1]. The present specimen was fabri-
cated from one of a lot of 2-inch bars supplied by Corning
Glass Works to Dr. D. C. Ginnings for measurements of ther-
mal diffusivity, which are under way in the NBS Heat Measure-
ments Section, 3.02. A specimen was also prepared for
measurement of thermal conductivity in our metals apparatus [7];
preliminary results have been obtained which agree reasonably
well with the data presented in this report.

a. Description of Specimen

The specimen used for these determinations was in the
form of a cylinder 2.540 cm in diameter and 1.269 cm in
length. The specimen was fabricated from the same bar used
to prepare the specimen for the NBS metals apparatus. The
density of the specimen material was 2.601 g/cm^3 (value sup-
plied by Corning). The ends of the specimen were optically
polished so as to be flat to within 1/10 light fringe (approx.
$3x10^{-6}$ cm).

b. Test Procedure

The specimen was placed between the platinum-rhodium hot
and cold bars, as shown in figure 1. (The hot and cold bars
had been optically polished to be flat to within 1 light
fringe.) Temperatures along the Pyroceram specimen were deter-
mined by means of three 0.20-mm butt-welded platinum-10% rho-
dium:platinum thermocouples pressed into 0.15 mm grooves in
the convex surface of the specimen. These grooves were equally
spaced, one being at the mid-plane of the specimen and the
others 0.50 cm above and below the mid-plane.

Thermal conductivity measurements were made in increasing
order of temperature from 200° to 500°C at 100-degree inter-
vals. The specimen was then heated to 600°C, but no data were
taken (due to a break in the water mains which supplied the
cooling water); the specimen was then cooled to room tempera-
ture. On second heating, measurements were made at 300°C and
at 100 degree intervals from 600° to 1000°C. The specimen was
held at 1000°C for about 275 hours, several sets of data being

taken during this time. Measurements were then made in decreasing order of temperature at 900°, 600°, and 300°C. Each conductivity determination involved an "isothermal" test and a "gradient" test.

c. Results of Thermal Conductivity Tests

The thermal conductivity and thermal resistivity of the Pyroceram specimen, as determined by simultaneous solution of the various pairs of tests, are shown in figure 9. The solid lines shown are given by

$$w = 1/k = 26.7 + 9.7(\frac{T}{1000}) \quad , \quad (23)$$

where w is thermal resistivity (cm deg C/watt), k is thermal conductivity (watt/cm deg C), and T is temperature (°C). Equation (23) is the linear equation of least-mean-squares fit to the thermal resistivity values obtained from the first and second heating cycles. The percent deviations of the experimental resistivity values from the smooth curve are shown in figure 10. The points connected by a line (or in close juxtaposition) represent the individual values obtained in each pair of tests for the two thermocouple spans in the specimen. The horizontal displacement of two connected points is indicative of the temperature gradient in the specimen; for most of the tests this gradient was 30 to 45 deg C/cm[5]. The dotted lines in figure 10 bound the region plus or minus two standard percent deviations (estimated; first and second heating only).

The data points obtained on second cooling are in substantial agreement with the data taken before the specimen was held at 1000°C, thus indicating that no appreciable change in the thermal conductivity of Pyroceram 9606 occurred as a result of this heat treatment.

5. DISCUSSION

The results presented above indicate that the high temperature absolute cut-bar apparatus is capable of very good precision. Comparison of the thermal conductivity values obtained for Inconel 702 with independent values obtained by

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5. Exceptions to this are as follows:
    First heating - 200°C, 20 deg C/cm (both pairs);
                     300°C, 20 deg C/cm (one pair);
    Second heating- 600°C, 60 deg C/cm (one pair);
                   600°C, 10 deg C/cm (one pair);
                 1000°C, 15 deg C/cm (two pairs);
                 1000°C, 70 deg C/cm (one pair).

other methods are indicative of the accuracy of the method, at least for that material. Preliminary results for Pyroceram obtained using the NBS metals apparatus are in good agreement with the values presented in Section 4.3.c. Additional analysis of the data presented in Section 4 will be performed and minor adjustments in the values will probably be made. However, it is felt that the data given are substantially correct.

The ultimate objective of this investigation is the provision of samples for use by other laboratories as thermal conductivity reference specimens in connection with their measurements on solid semi-conductors. Of equal importance, it is felt, is the proper use of such standards.

The problems encountered in the design and operation of the absolute cut-bar apparatus have pointed out some of the difficulties arising in measurements of this type on small samples. The two most serious difficulties are due to the thermal resistances at the contacting surfaces of the specimen and the extraneous exchange of heat with the surrounding insulation. In order to avoid the problem of attempting to measure contact resistance, it is recommended that thermocouples be placed in the specimen not too near its contact surfaces.

A detailed analysis of heat flow in the insulation of a simplified cut-bar apparatus was presented by this author at the Invitational Conference on Thermal Conductivity Methods held at Battelle Memorial Institute, Columbus, Ohio, on October 26-28, 1961. In view of the similarity of this analysis to that used for the NBS absolute cut-bar apparatus, this paper, "Thermal Guarding of Cut-Bar Apparatus," was reproduced at the end of a previous report [5].

Many laboratories are currently utilizing various forms of a comparative cut-bar apparatus for their thermal conductivity measurements. A typical example would be the apparatus of Francl and Kingery [12]. It was shown by Laubitz [13] that this type of apparatus is very sensitive to the alignment of its components. As has been pointed out, shunting heat flows through the insulation are also a serious problem in an apparatus of this type if the specimen and meter bars are of different conductivities.

It was shown in the paper at the end of reference [5] that the fractional error due to shunting of heat through the insulation is given quite closely by

$$-\varepsilon = K_1 \left(\frac{1}{K_m} - \frac{1}{K_s}\right) D \qquad , \qquad (24)$$

for a comparative cut-bar apparatus with meter bars of conductivity K_m, a specimen of conductivity K_s, insulation of conductivity K_i, and where D is a geometrical factor. The effect of varying specimen thermal conductivity for different meter bars is shown in greater detail in figure 11. Here the coefficient conductivity-term of equation (24),

$$K_i \left(\frac{1}{K_m} - \frac{1}{K_s} \right) \quad ,$$

is plotted against K_s, the thermal conductivity of the specimen, for four values of K_m, the thermal conductivity of the meter bars. The thermal conductivity of the insulation is held fixed at 0.001 w/cm-C. The quantity plotted goes through zero at $K_s = K_m$, approaches $-\infty$ as K_s becomes quite small, and asymptotically approaches K_i/K_m as K_s becomes large.

A typical geometrical factor, $D(\mu)$, would probably not exceed a value of 2.5. If the vertical scale in figure 11 were multiplied by 2.5, each scale division, 0.02, would become 0.05, or 5 percent. Hopefully, the geometrical factor might be made as small as 0.5 or 1.0, so that each vertical scale division would become 1 or 2 percent, respectively.

If both the specimen and the meter bars have at least one hundred times the thermal conductivity of the insulation, the choice of a particular meter bar is not critical. If the specimen to be measured has a thermal conductivity on the order of ten times that of the insulation, or less, the choice of a suitable meter bar becomes quite important.

It can be seen from Figure 11 that the conductivity of the meter bars should be near the lower end of the range to be covered, if it is desired to measure a wide range of specimen thermal conductivities, utilizing a single pair of meter bars. If

$$K_m = \frac{2(K_s)_{max} \, (K_s)_{min}}{(K_s)_{max} + (K_s)_{min}} \quad , \tag{25}$$

where $(K_s)_{max}$ and $(K_s)_{min}$ are the maximum and minimum specimen thermal conductivities to be measured, then the maximum error to be expected within the range is

$$\pm \frac{K_i}{2} \left[\frac{1}{(K_s)_{max}} - \frac{1}{(K_s)_{min}} \right] D \quad . \tag{26}$$

For relatively large $(K_s)_{max}$, equation (26) reduces to

$$\pm \frac{1}{2} \frac{K_1}{(K_S)_{min}} D(\mu) \qquad (27)$$

It is of interest to investigate numerically the signi-
ficances of equations (25) and (26). Table 4 gives several
ranges of thermal conductivity, the preferred meter bar con-
ductivity for each range, and the maximum error to be expected
for a given geometrical factor (1.0) and insulation thermal
conductivity (0.001 w/cm-C).

TABLE 4

Maximum Error for Various Ranges of Specimen
Thermal Conductivity

K_S		optimal K_m	maximum error in K_S range
minimum w/cm-C	maximum w/cm-C	w/cm-C	± %
0.005	0.01	0.0067	5.0
.01	.015	.0120	1.7
.01	.02	.0133	2.5
.01	.05	.0167	4.0
.01	.10	.0182	4.5
.01	1.00	.0198	5.0
.05	.10	.0667	.50
.05	.50	.0909	.90
.10	.50	.167	.40
.10	1.00	.182	.45
.10	10.00	.198	.50
1.00	10.00	1.82	.045

The value assumed above for the thermal conductivity of
the insulation (0.001 w/cm deg C) is probably a fairly typi-
cal value; at high temperatures, however, the value might be
considerably higher, thus causing a proportionately larger
error. The value assumed for the geometrical factor (1.0)
may also be low by a factor of two or more under some condi-
tions. Thus, the maximum errors obtained in an actual case
could be much larger than those given in table 4. Note that
the errors are particularly large in the range of maximum
interest for thermoelectric devices (0.01 to 0.05 watt/cm deg C).

The effects of these unwanted heat flows can be avoided
by means of a suitable calibration, if suitable thermal conduc-
tivity reference specimens can be made available. The best

use of such reference specimens is discussed in another paper
presented at the above mentioned conference. In his paper
"Current NBS Steady-State Thermal Conductivity Methods,"
H. E. Robinson, Chief of the NBS Heat Transfer Section, con-
cluded by saying:

"The idea of a thermal conductivity reference standard
is manifest. Nevertheless, such standards involve other
problems than merely those of selecting suitable materials
and determining their conductivity as accurately as possible.

"For example, the best use of a reference material is
to use it as a substitute specimen, as is done for instance
in precise determinations of electrical resistance. When
the reference is used in this way in a particular apparatus,
it is presumably subject to the same unwanted heat flows,
resulting from what might be termed the accessory conditions
of the apparatus, as would be a test specimen of equal con-
ductivity. If the reference is thus used to calibrate a
metering device of some sort, as it would be in a comparative
type of testing apparatus, the calibration of the meter would
inherently contain the effects of these perturbations. This
consideration is of special importance in the case of heat
flow measuring equipment, because there is no perfect thermal
insulation or guarding to eliminate unwanted heat flows.
Such use of the reference as a substitute specimen carries
with it, however, the strict requirement that the accessory
conditions of the apparatus be duplicable in ordinary tests,
as in the calibrating tests. Thus, in this sense, the best
use of a reference standard involves the design of the appa-
ratus to be calibrated with it, in regard to the precision
with which the accessory conditions can be controlled and
duplicated.

"As an illustration, it would not be the best use of a
reference material of known conductivity to employ it as the
heat flow meters in a series arrangement such as meter-
specimen-meter. The better use would be to employ for the
metering bodies some suitable material, and obtain a cali-
bration for them by using the reference in place of the speci-
men. If reference substitute specimens covering a range of
conductivities were used, and accessory conditions were ade-
quately reproduced, it is probable that test measurements on
unknown specimens of conductivities within the range covered
by the references could be made with results not seriously
inferior in absolute value to those of the reference speci-
mens...."

In order to adequately calibrate a thermal conductivity
measuring device for use on thermoelectric materials, it

would appear desirable to have available at least three
reference substitute specimens: a) one having a thermal
resistivity near the upper end of the range found for ther-
moelectric materials, b) one near the lower end of this
range, and c) one somewhere near the middle of this range.
All such reference standards should be homogeneous and iso-
tropic, stable in air at elevated temperatures, opaque to
thermal radiation, and should not be excessive in cost.

The nickel-chromium alloy, Inconel 702, for which
results were presented above, appears to be suitable as a
reference standard having a thermal conductivity near the
upper limit of that of most thermoelectric materials of
interest. The data presented in table 1 indicate that the
thermal conductivity of this material is well-known over the
temperature range from -150° to 1200°C. Samples of this
alloy (cut from the same plate as were the NBS specimens)
have been sent to Dr. R. W. Powell of the National Physical
Laboratory (Teddington, Middlesex, England), to Dr. M. J.
Laubitz of the National Research Council (Ottawa, Ontario,
Canada), and to Dr.-Ing. Karl-Heinz Bode of the Physikalisch-
Technische Bundesanstalt (Braunschweig, West Germany). Sam-
ples have also been provided to a few selected laboratories
in this country. In conjunction with thermal conductivity
measurements, many of these laboratories will also conduct
electrical resistivity determinations.

The NBS Heat Transfer Section intends to measure the
electrical resistivity of Inconel 702 from -195° to 1200°C
or higher with particular attention to the effects of heat
treatment. The thermoelectric power of this alloy will also
be measured over a wide temperature range. Photomicrographs
are being prepared of the solution-annealed alloy and of a
sample cut from the thermal conductivity specimen after com-
pletion of testing to 1200°C in the high temperature absolute
cut-bar apparatus. It is felt that samples of NBS Inconel
702 can soon be made available to interested laboratories for
use as reference specimens.

Microcrystalline glass, Pyroceram 9606, appears quite
promising for use as a reference standard having a thermal
conductivity similar to that of many thermoelectric materials.
Measurements on this material have been completed in the NBS
metals apparatus over the range 100° to 650°C. The data have
not been completely analyzed, but appear to be in substantial
agreement with the values obtained in the high temperature
absolute cut-bar apparatus. These measurements will be
extended to -150°C if analysis indicates such to be feasible.
Thermal diffusivity of Pyroceram 9606 is being determined by
the NBS Heat Measurements Section. In view of the promising

results obtained thus far with Pyroceram 9606, it is considered worthwhile to discuss with the manufacturer the possibility of obtaining an adequate stock from which, after the necessary measurements, samples suitable for distribution to other laboratories can be cut.

The selection of a suitable reference standard having a thermal conductivity lower than that liable to be encountered in thermoelectric materials poses a rather difficult problem. It is quite desirable that any material selected be available in a wide variety of sizes and shapes, so that thermal conductivity specimens can be prepared for test by conventional methods. In principle, a lower thermal conductivity should be attainable in an electrical insulator than in a semiconductor, since there is no electronic component of thermal conductivity in the former. Furthermore, an amorphous solid, in general, will have a lower thermal conductivity than a crystalline material possessing long-range order. Thus, one is led to the conclusion that a glassy material would be a suitable reference standard for this range of thermal conductivity.

Fused silica (quartz) has been proposed as a thermal conductivity standard. While there is a great deal of discrepancy among some of the older data in the literature, some of the more recent determinations [14,15,16] are in better agreement, indicating that the room temperature value for the thermal conductivity of fused silica is about 0.013 to 0.015 watt/cm deg C. Above about 400°C, in addition to heat transfer by vibrational modes, heat is transferred through silica by thermal radiation. This radiative transfer rapidly becomes quite large [17,18,19] so that at elevated temperatures the thermal conductivity of fused silica becomes a rather ambiguous property.

Pyrex glass (7740, Corning) has a thermal conductivity somewhat lower than that of fused silica. At room temperature the value is about 0.010 to 0.012 watt/cm deg C [1,16, 18,20,21,22]. Unfortunately, Pyrex also becomes transparent to thermal radiation above about 400°C. In order to confirm measurements made in the prototype absolute cut-bar apparatus [1], a specimen of Pyrex 7740 has been prepared for testing in the high temperature absolute cut-bar apparatus. The specimen is identical in size and shape to the Pyroceram specimen described in Section 4.3. The flat surfaces of this specimen have been coated with gold, in order to minimize radiative heat transfer.

Additional efforts are being directed toward the selection of a suitable reference material having a thermal conductivity similar to that of fused silica or Pyrex. Consideration is being given to a glass containing colorants to increase opacity.

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6. REFERENCES

1. D. R. Flynn and H. E. Robinson, Thermal conductivity of semiconductive solids; method for steady-state measurements on small disc samples, NBS Interim Technical Report 7135, covering period Feb. 23, 1959, to Mar. 31, 1961.

2. E. D. West and D. C. Ginnings, Automatic temperature regulation and recording in precision adiabatic calorimetry, Rev. of Sci. Instru. 28, 1070-1074 (1957).

3. W. F. Roeser, Thermoelectric thermometry, J. Appl. Phys. 11, 404-405 (1940); also in Temperature, its Measurement and Control in Science and Industry, 202 (Reinhold Publishing Corp., New York, New York, 1941).

4. D. R. Flynn, A radial flow apparatus for determining the thermal conductivity of loose-fill insulations to high temperatures (to be published).

5. D. R. Flynn, Thermal conductivity of semiconductive solids; method for steady-state measurements on small disk reference samples, NBS Technical Progress Report 7367 for period July 1 to Sept. 30, 1961.

6. W. F. Roeser, ob. cit., 389-390; 181-182.

7. T. W. Watson and H. E. Robinson, Thermal conductivity of some commerical iron-nickel alloys, ASME Jour. of Heat Transfer, 403-408 (Nov. 1961).

8. D. R. Flynn, D. A. Didion, and C. I. Siu, A steam calorimeter apparatus for determination of the thermal conductivity of refractory solids (to be published).

9. R. W. Powell and R. P. Tye, Thermal and electrical conductivities of nickel-chromium (nimonic) alloys, The Engineer, 729-732 (April 29, 1960).

10. S. D. Stookey, Glass-ceramics, Chem. Eng. News 39, 116 (June 19, 1961).

11. S. D. Stookey, Glass-ceramics, Mech Eng. 82, 65 (Oct. 1960).

12. J. Francl and W. D. Kingery, Thermal conductivity: IV, apparatus for determining thermal conductivity by a comparative method, J. Am. Ceram. Soc. 37, 80 (1954).

13. M. J. Laubitz, On measurement of thermal conductivity at high temperatures, Can. J. Phys. 39, 1029 (1961).

14. E. H. Ratcliffe, Thermal conductivities of fused and crystalline quartz, Brit. J. Appl. Phys. 10, 22 (1959).

15. E. D. Devyamkova, A. V. Pemrov, I. A. Smirnov, and B. Ya. Moizhes, Fused quartz as a model material in thermal conductivity measurements, Soviet Physics, Solid State, 2, 681 (Oct. 1960). (Translated from Fizika Tverdogo Tela, 2, 738 (Apr. 1960)).

16. W. D. Kingery, Thermal conductivity: XII, temperature dependence of conductivity of single-phase ceramics, J. Amer. Ceram. Soc. 38, 251 (1955); and Thermal conductivity: XIV, conductivity of multicomponent systems, J. Amer. Ceram. Soc. 42, 617 (1959).

17. W. D. Kingery, Heat conductivity processes in glass, J. Amer. Ceram. Soc. 44, 302 (1961).

18. C. F. Lucks, H. W. Deem, and W. D. Wood, Thermal properties of six glasses and two graphites, Amer. Ceram. Soc. Bull. 39, 313 (1960).

19. K. L. Wray and T. J. Connolly, Thermal conductivity of clear fused silica at high temperatures, J. Appl. Phys. 30, 1702 (1959).

20. R. W. B. Stephens, The temperature variation of the thermal conductivity of Pyrex glass, Phil. Mag. 14, 897 (1932).

21. F. Birch and H. Clark, The thermal conductivity of rocks and its dependence upon temperature and composition, Amer. J. Sci. 238, 529 (1940).

22. A. R. Challoner, H. A. Gundry, and R. W. Powell, A radial heat-flow appratus for liquid thermal conductivity determinations, Proc. Roy. Soc. A245, 259 (1958).
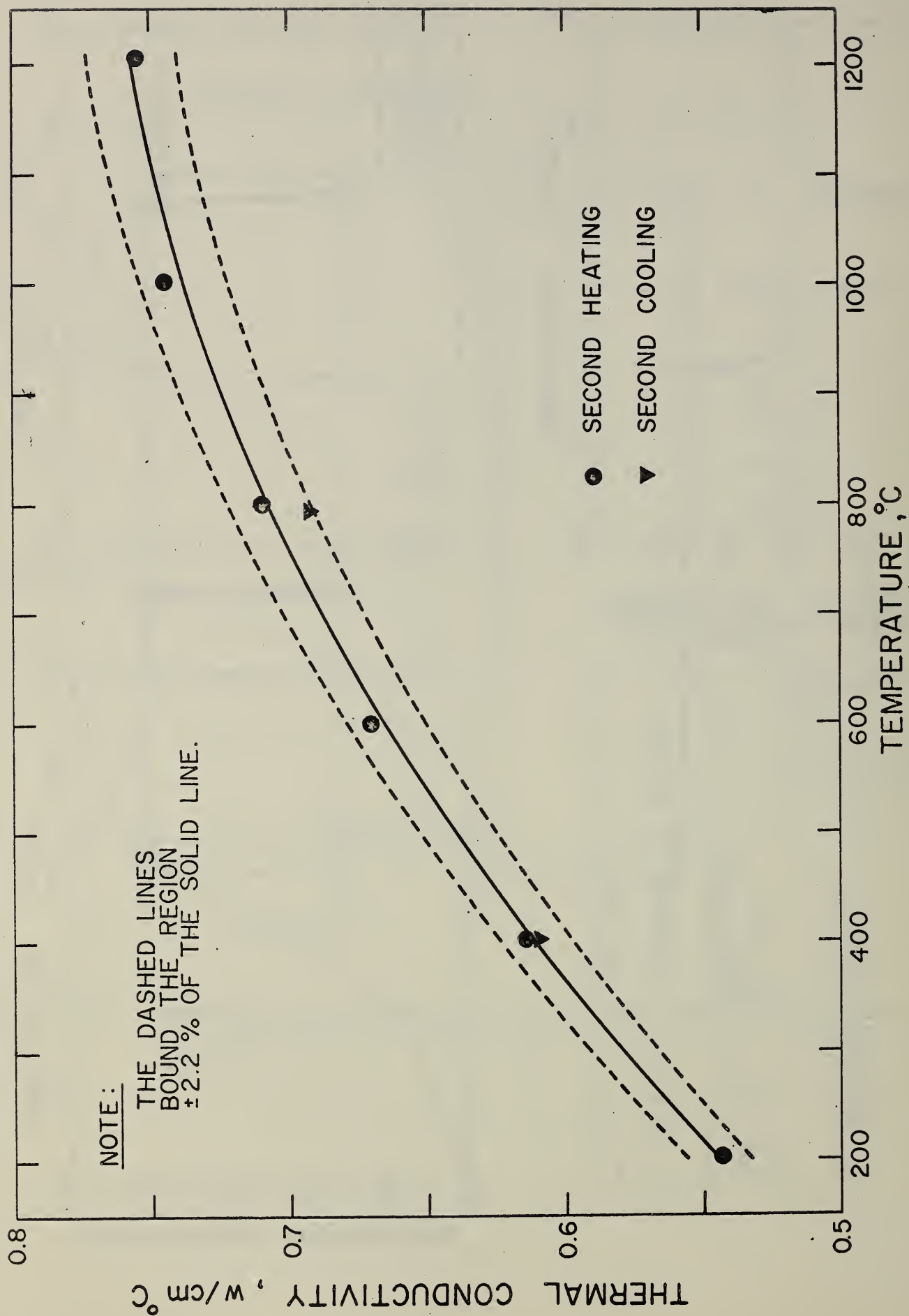
Figure 3. Thermal conductivity of a 60% platinum-40% rhodium alloy.
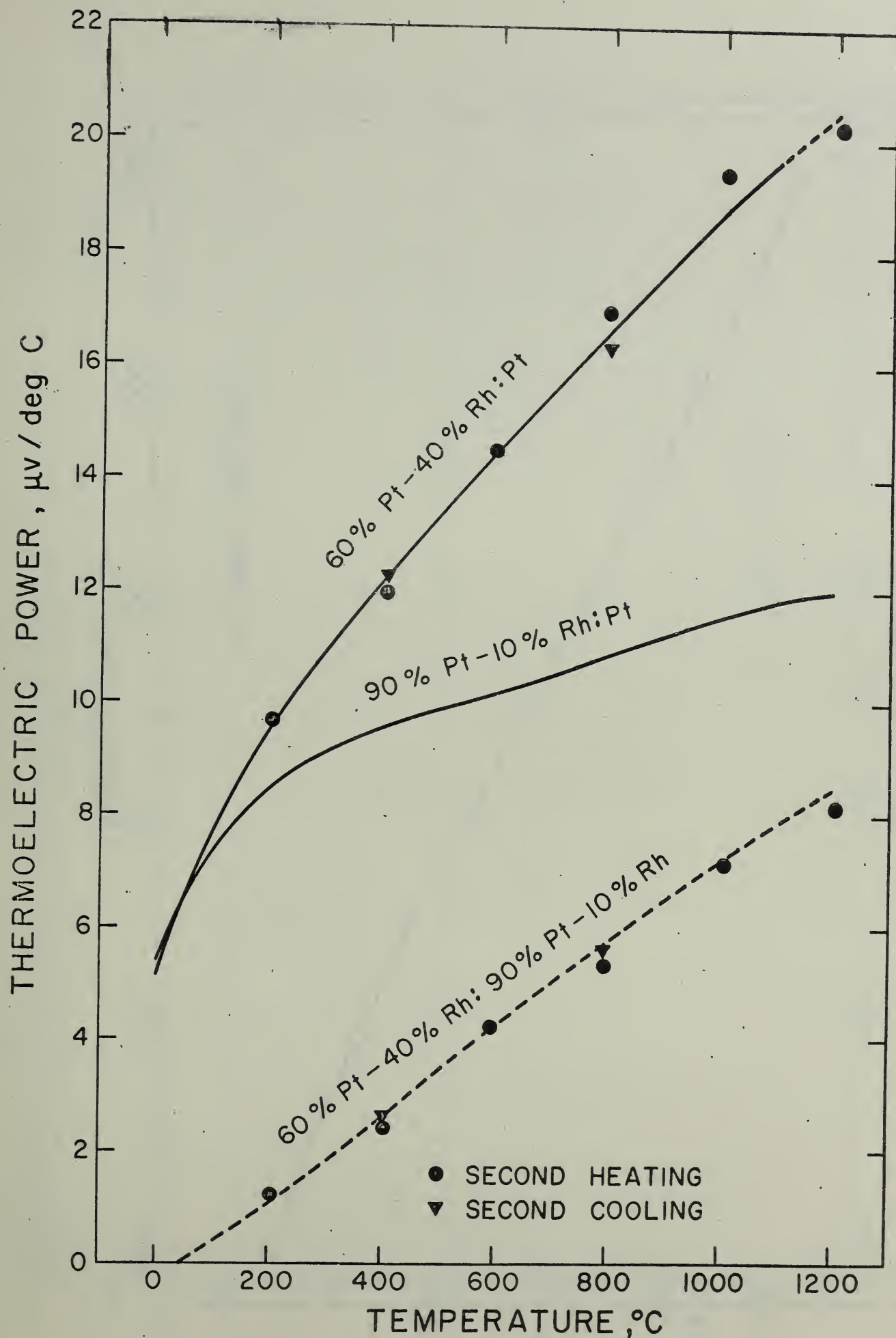
Figure 4.   Thermoelectric power of platinum-40% rhodium and
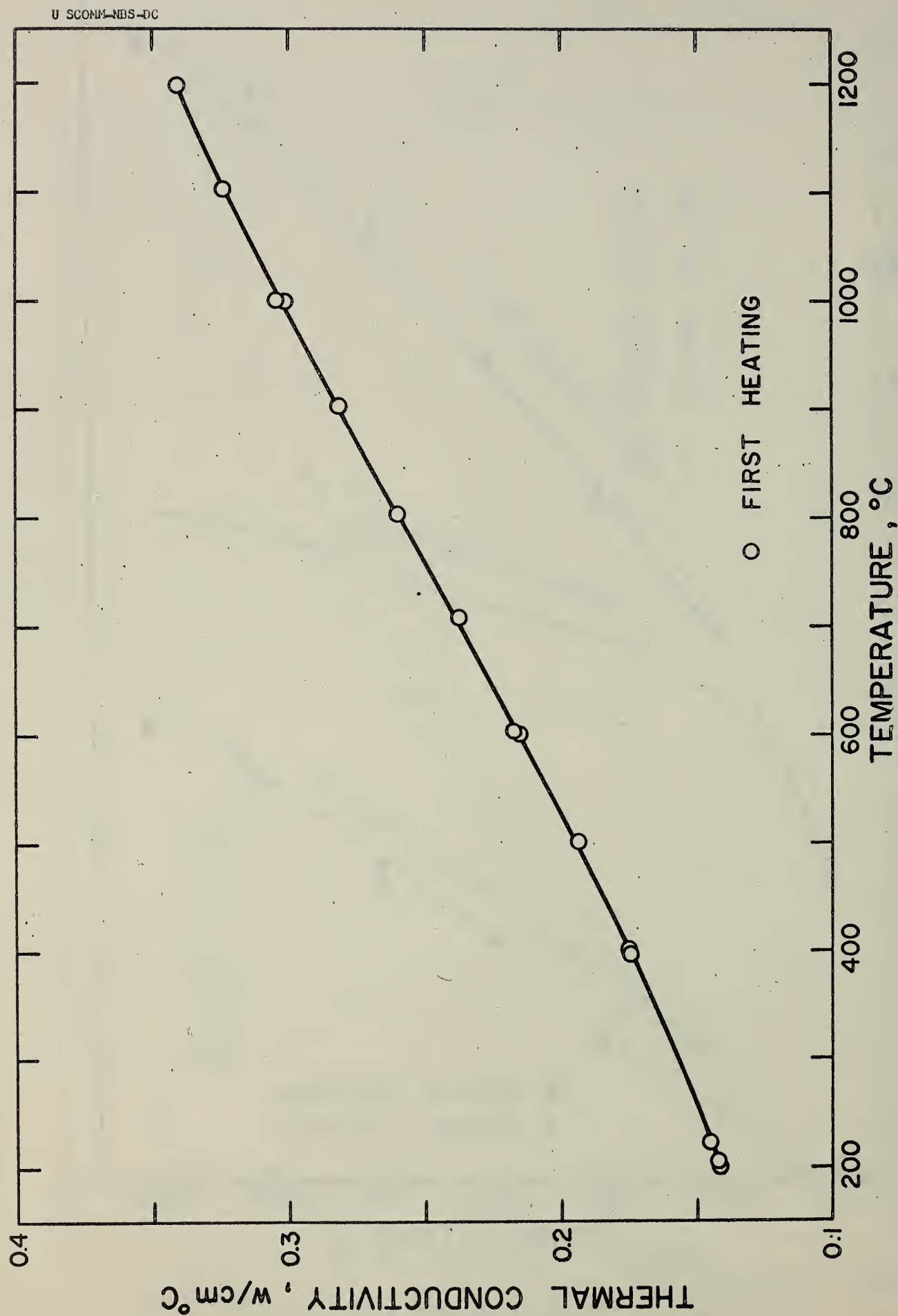platinum-10% rhodium against pure platinum.

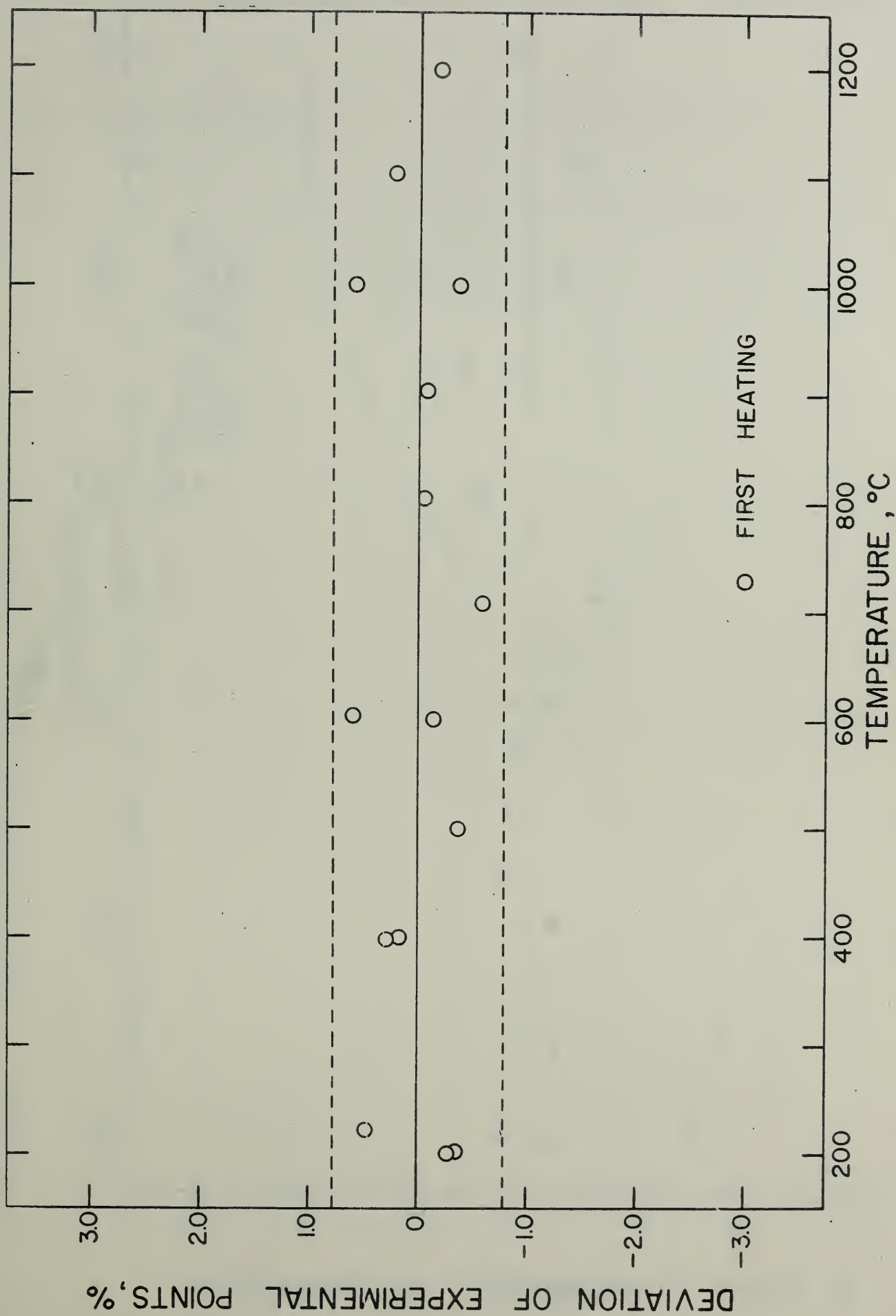Figure 5. Thermal conductivity of solution-annealed Inconel 702.

Figure 6. Departures of the thermal conductivity data for solution-annealed
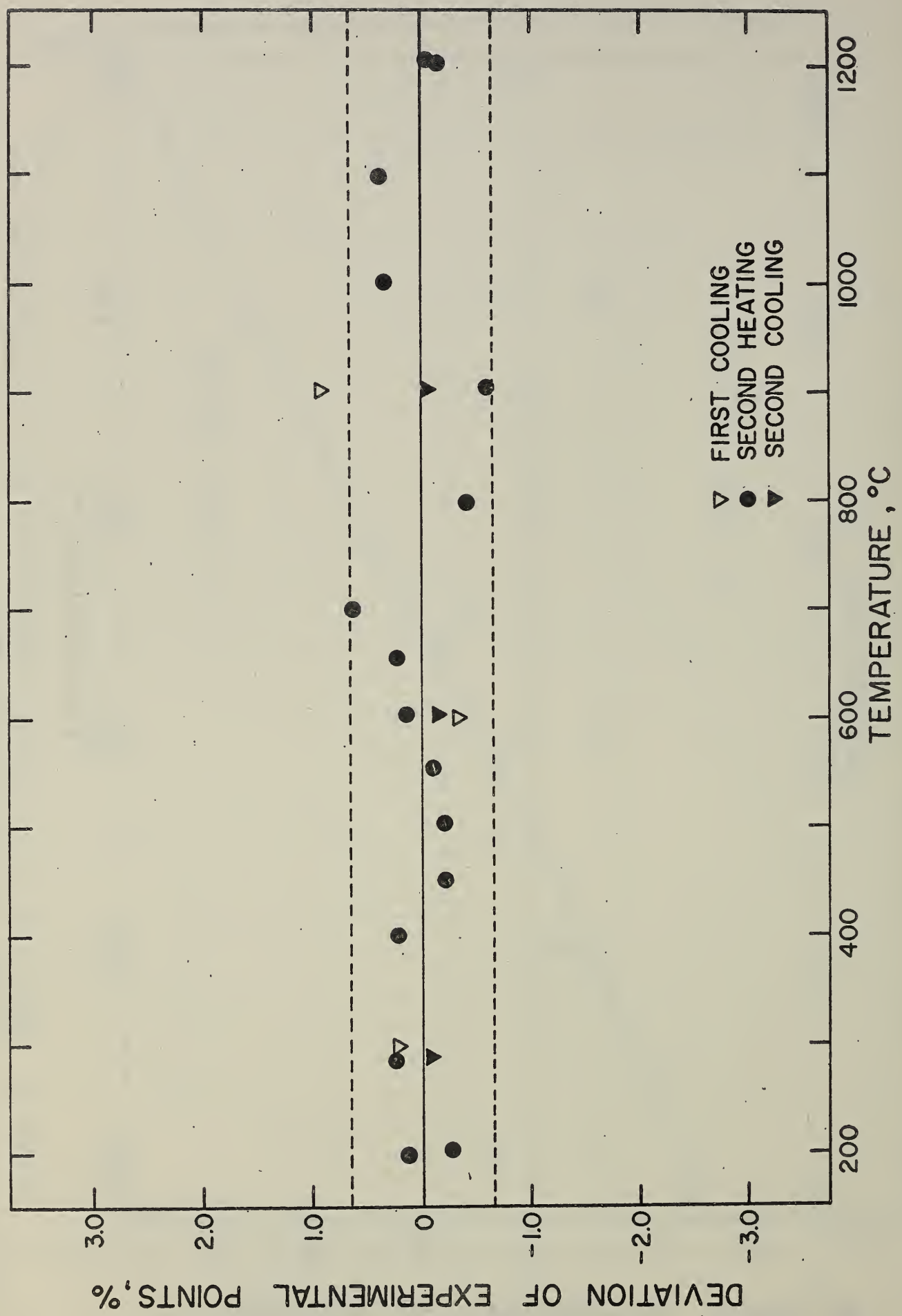Inconel 702 from a smooth curve.

Figure 7. Departures of the thermal conductivity data for age-hardened Inconel 702 from a smooth curve.
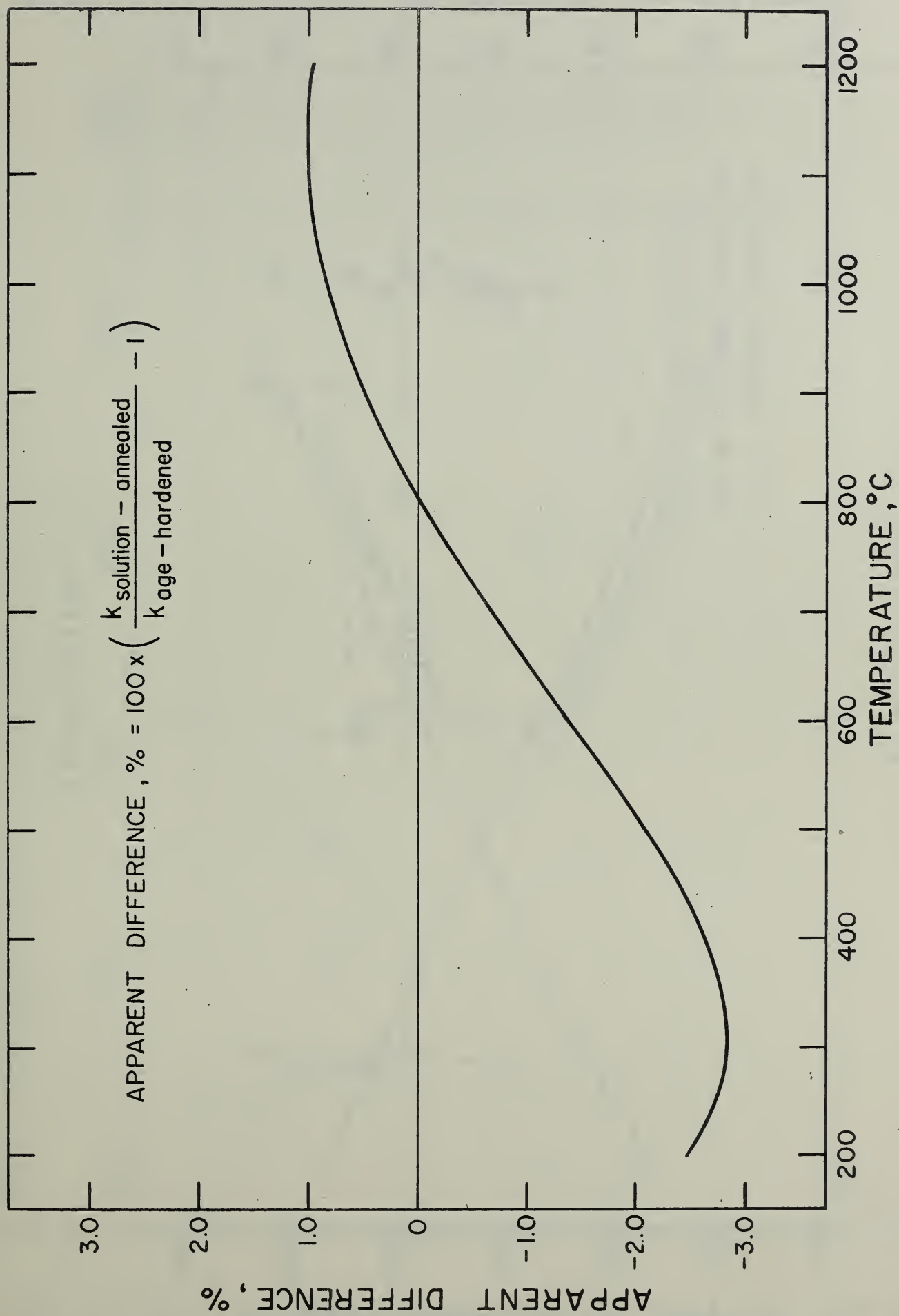
Figure 8. Apparent difference between the thermal conductivity of solution-annealed Inconel 702 and that of the age-hardened alloy.
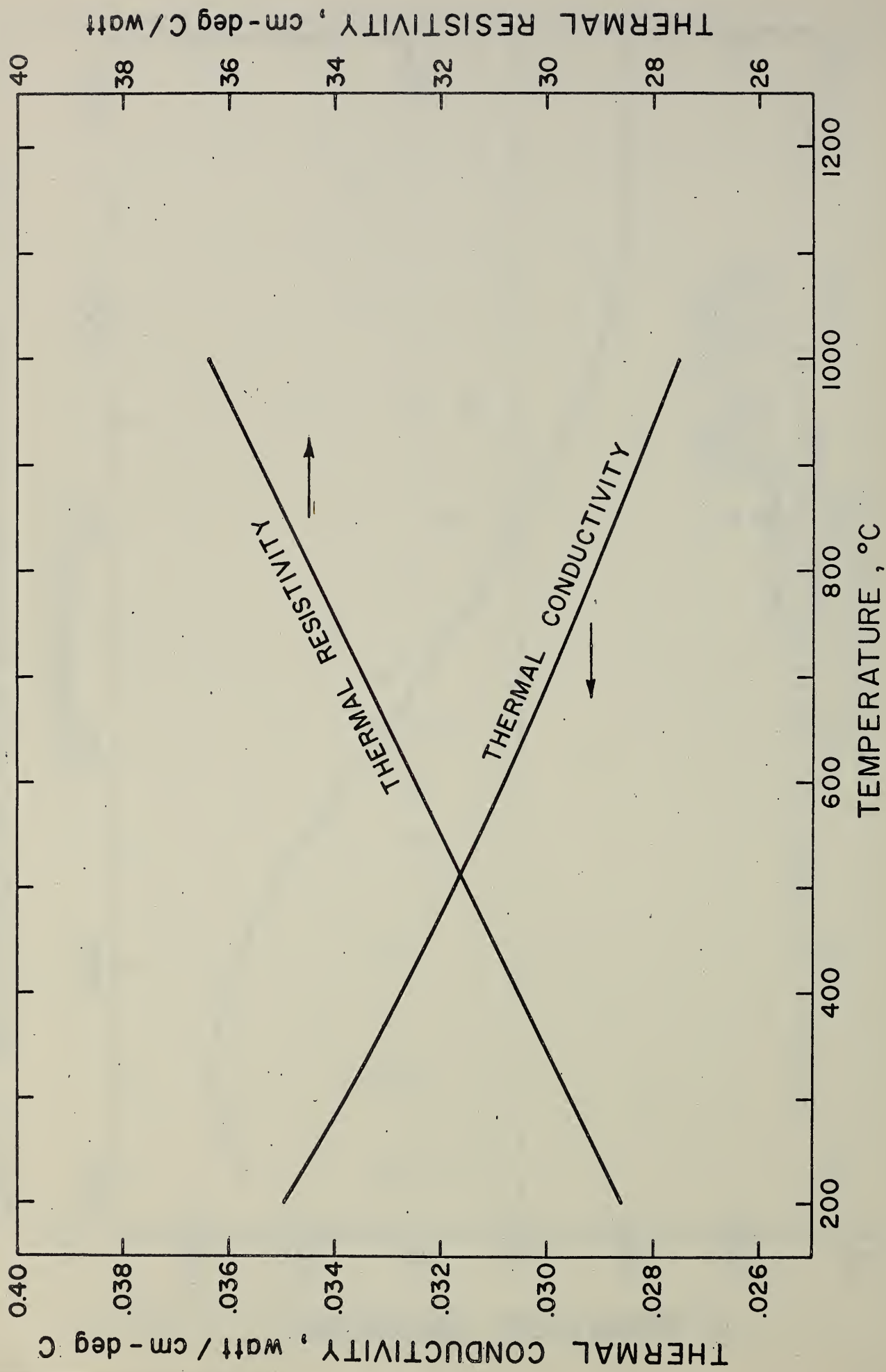
Figure 9. Smoothed values for the thermal conductivity and thermal resistivity of Pyroceram 9606.
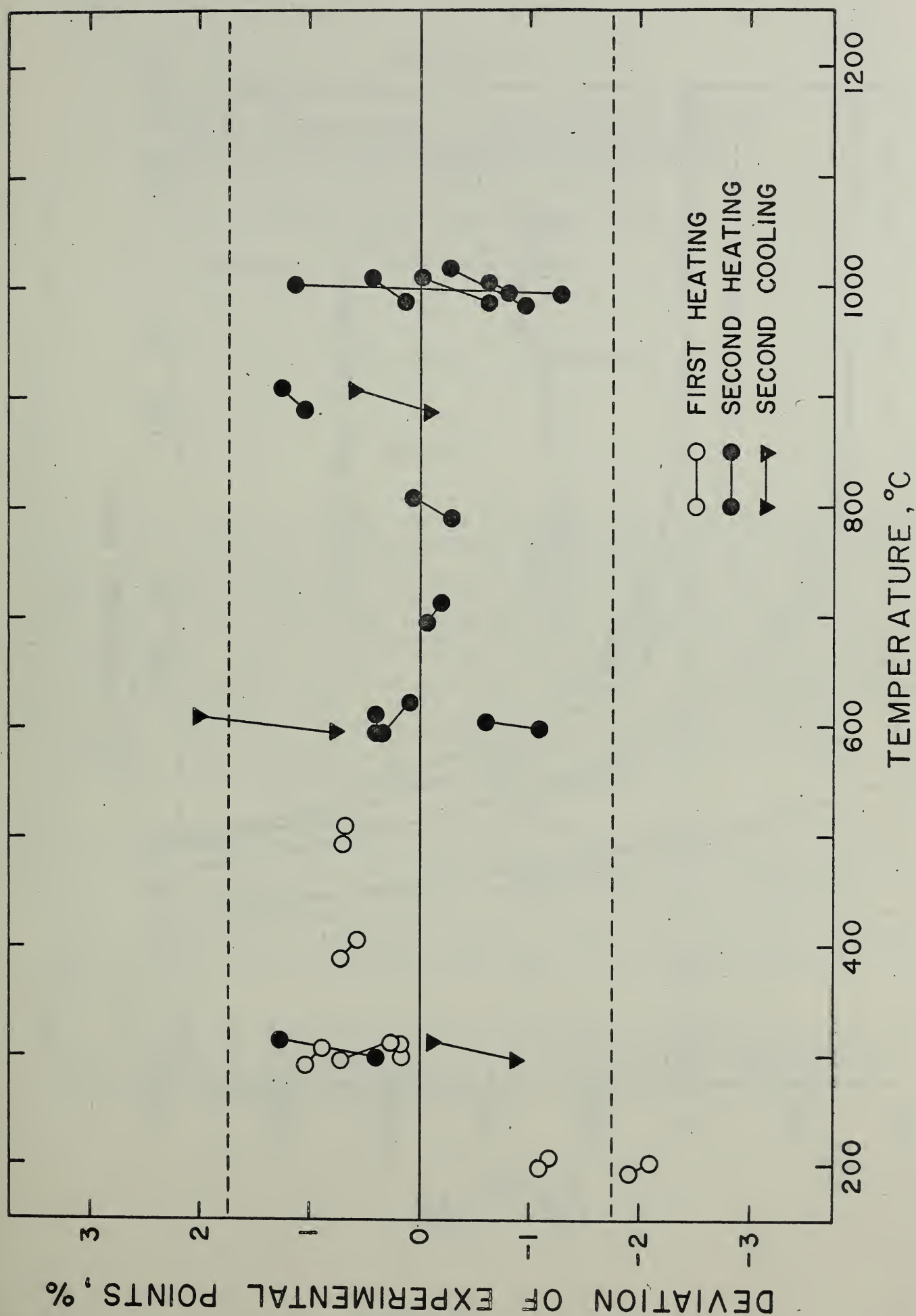
Figure 10. Departures of the thermal resistivity data for Pyrcceram 9606 from a
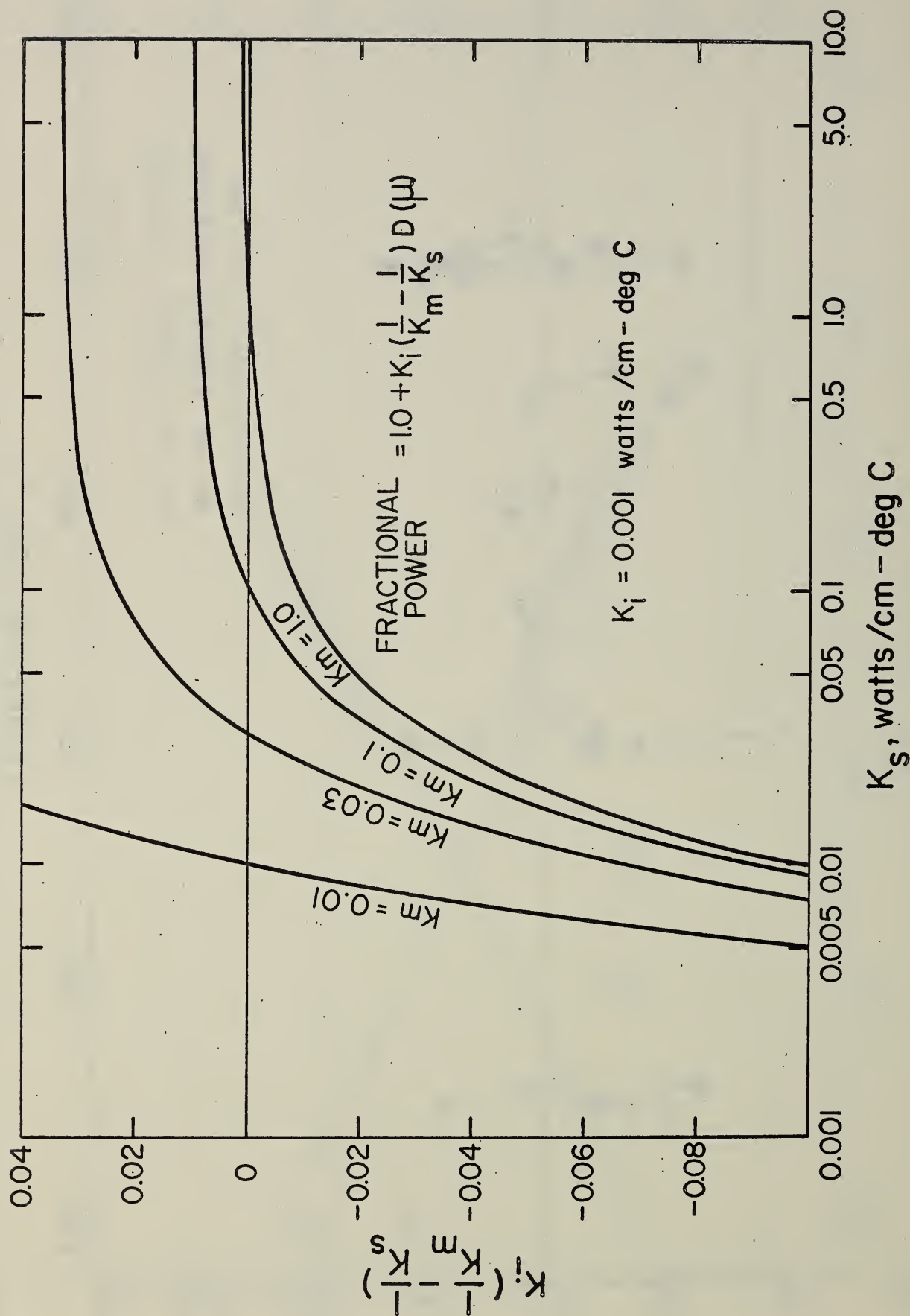smooth curve.

Figure 11. Effect of thermal conductivity on the fractional power
change in a comparative cut-bar apparatus.

APPENDIX A

THERMAL CONDUCTIVITY OF SEMICONDUCTIVE SOLIDS;
METHOD FOR STEADY-STATE MEASUREMENTS ON
SMALL DISC REFERENCE SAMPLES

Interim Technical Report 7135
Covering Period
February 23, 1959, to March 31, 1961

by

D. R. Flynn and H. E. Robinson

ABSTRACT

An absolute cut-bar method of measuring the thermal con-
ductivity of solids is described, suitable for small specimens
of semiconductive materials. Measurements have been made at
temperatures from 100° to 800°C on Pyrex, Pyroceram, and a
nickel-chrome alloy, and representative tentative results are
given. The data for the nickel-chrome alloy, over the common
temperature range 130° to 600°C, agree with the smoothed data
from measurements made on the same material by an independent
absolute method, with a standard deviation of 0.7 percent.
The data for Pyrex and Pyroceram may be subject to errors
because of the uncertainties introduced by thermal contact
resistance at the surfaces of the specimens.

It is shown that the use of a matched guard in a cut-bar
apparatus does not reduce extraneous heat exchanges between
the bars and specimen and the surrounding powder insulation to
the small magnitude desirable for good accuracy of measure-
ment. A mathematical analysis of the system indicates a
superior guarding condition which greatly reduces these extra-
neous heat flows, and which was used in the measurements
mentioned.

Using the knowledge acquired by these investigations, a
final model of the apparatus is being built for measurements
on small specimens (1/2-in. by 1-in. diameter discs) at tem-
peratures in excess of 1200°C.

THE NATIONAL BUREAU OF STANDARDS

The scope of activities of the National Bureau of Standards at its major laboratories in Washington, D.C., and Boulder, Colorado, is suggested in the following listing of the divisions and sections engaged in technical work. In general, each section carries out specialized research, development, and engineering in the field indicated by its title. A brief description of the activities, and of the resultant publications, appears on the inside of the front cover.

WASHINGTON, D. C.

Electricity. Resistance and Reactance. Electrochemistry. Electrical Instruments. Magnetic Measurements. Dielectrics. High Voltage.

Metrology. Photometry and Colorimetry. Refractometry. Photographic Research. Length. Engineering Metrology. Mass and Scale. Volumetry and Densimetry.

Heat. Temperature Physics. Heat Measurements. Cryogenic Physics. Equation of State. Statistical Physics.

Radiation Physics. X-ray. Radioactivity. Radiation Theory. High Energy Radiation. Radiological Equipment. Nucleonic Instrumentation. Neutron Physics.

Analytical and Inorganic Chemistry. Pure Substances. Spectrochemistry. Solution Chemistry. Standard Reference Materials. Applied Analytical Research. Crystal Chemistry.

Mechanics. Sound. Pressure and Vacuum. Fluid Mechanics. Engineering Mechanics. Rheology. Combustion Controls.

Polymers. Macromolecules: Synthesis and Structure. Polymer Chemistry. Polymer Physics. Polymer Characterization. Polymer Evaluation and Testing. Applied Polymer Standards and Research. Dental Research.

Metallurgy. Engineering Metallurgy. Microscopy and Diffraction. Metal Reactions. Metal Physics. Electrolysis and Metal Deposition.

Inorganic Solids. Engineering Ceramics. Glass. Solid State Chemistry. Crystal Growth. Physical Properties. Crystallography.

Building Research. Structural Engineering. Fire Research. Mechanical Systems. Organic Building Materials. Codes and Safety Standards. Heat Transfer. Inorganic Building Materials. Metallic Building Materials.

Applied Mathematics. Numerical Analysis. Computation. Statistical Engineering. Mathematical Physics. Operations Research.

Data Processing Systems. Components and Techniques. Computer Technology. Measurements Automation. Engineering Applications. Systems Analysis.

Atomic Physics. Spectroscopy. Infrared Spectroscopy. Far Ultraviolet Physics. Solid State Physics. Electron Physics. Atomic Physics. Plasma Spectroscopy.

Instrumentation. Engineering Electronics. Electron Devices. Electronic Instrumentation. Mechanical Instruments. Basic Instrumentation.

Physical Chemistry. Thermochemistry. Surface Chemistry. Organic Chemistry. Molecular Spectroscopy. Elementary Processes. Mass Spectrometry. Photochemistry and Radiation Chemistry.

Office of Weights and Measures.

BOULDER, COLO.

Cryogenic Engineering Laboratory. Cryogenic Equipment. Cryogenic Processes. Properties of Materials. Cryogenic Technical Services.

CENTRAL RADIO PROPAGATION LABORATORY

Ionosphere Research and Propagation. Low Frequency and Very Low Frequency Research. Ionosphere Research. Prediction Services. Sun-Earth Relationships. Field Engineering. Radio Warning Services. Vertical Soundings Research.

Radio Propagation Engineering. Data Reduction Instrumentation. Radio Noise. Tropospheric Measurements. Tropospheric Analysis. Propagation-Terrain Effects. Radio-Meteorology. Lower Atmosphere Physics.

Radio Systems. Applied Electromagnetic Theory. High Frequency and Very High Frequency Research. Frequency Utilization. Modulation Research. Antenna Research. Radiodetermination.

Upper Atmosphere and Space Physics. Upper Atmosphere and Plasma Physics. High Latitude Ionosphere Physics. Ionosphere and Exosphere Scatter. Airglow and Aurora. Ionospheric Radio Astronomy.

RADIO STANDARDS LABORATORY

Radio Physics. Radio Broadcast Service. Radio and Microwave Materials. Atomic Frequency and Time-Interval Standards. Radio Plasma. Millimeter-Wave Research.

Circuit Standards. High Frequency Electrical Standards. High Frequency Calibration Services. High Frequency Impedance Standards. Microwave Calibration Services. Microwave Circuit Standards. Low Frequency Calibration Services.